BIOSORPTION OF COPPER (II) FROM AQUEOUS SOLUTION BY USING DRIED WATER HYACINTH *(Eicchornia Crassipes)*

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I declare that this dissertation entitled "*Biosorption of Copper (II) from Aqueous Solution by Using Dried Water Hyacinth (Eichhornia Crassipes)*" is the result of my own research except as cited in the references. The Dissertation has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ....
Name : ....
Date : ....

I dedicate this thesis to my family, without them none of this would have been worth the challenge…

Supportive parents;

Sulaiman Hj Daud and Nik Azizah Ibrahim

It is all because of you

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ABSTRACT

This paper presents the results of research on capability of water hyacinth (*Eichhornia crassipes*) as low cost biosorbent in removing Cu (II) from aqueous solution and to identify the optimum uptake of Cu (II) based on four parameters that are effect of adsorbent dosage, initial concentration, pH and time contact by biosorption which could be used as an alternative approach to remove Cu (II) from water or selected wastewater. A series of batch studies were conducted using different amount of *Eichhornia crassipes* (0.1 - 0.6 g), different concentration of Cu (II) solution range from 10 to 100 mg/L at various pH values and time, shaken with constant stirring speed of 120 rpm at room temperature. It was found that Cu (II) has removed about 58 % at 0.5 grams of *Eichhornia crassipes* and the optimum initial concentration is at 80 mg/L with removal of 64 %. The biosorption of Cu (II) is found occurred at acidic (62 %) as the availability of negatively charged groups at the biosorbent surface which is necessary for the sorption of metals to proceed and copper was highly removed at 40 min due to surface adsorption on the biomass. The experimental has proved that water hyacinth (*Eichhornia crassipes*) are capable in removing Cu (II) and good biosorbent as it is low cost and indirectly solved environmental problem made from this easily growth plants and biosorption is an efficient technology replacing other conventional method in treating the wastewater.

ABSTRAK

Kajian ini membentangkan hasil ujikaji tentang kebolehan keladi bunting (*Eichhornia crassipes*) sebagai penjerap bio kos rendah dalam menyingkirkan Cu (II) dari larutan cecair dan mengenalpasti pengambilan Cu (II) yang optimum berdasarkan empat pembolehubah iaitu kesan dari dos penjerap bio, kepekatan awal, pH dan masa bersentuhan melalui penjerapan bio yang mana boleh di gunakan sebagai pendekatan alternatif untuk singkirkan Cu (II) dari air atau air buangan yang terpilih. Sebuah siri terhadap bahagian penyelidikan telah dijalankan menggunakan dos keladi bunting yang berbeza (0.1 – 0.6 g), kepekatan larutan Cu (II) yang berbeza dari senggat 10 – 100 mg/L pada pelbagai nilai pH dan masa, dengan pengadukkan yang tetap pada 120 rpm pada suhu bilik. Telah didapati bahawa Cu (II) telah disingkir sebanyak 58 % pada 0.5 g keladi bunting dan kepekatan awal yang optimum adalah pada 80 mg/L dengan penyingkiran sebanyak 64 %. Penjerapan bio terhadap Cu (II) ini dikesan berlaku pada keadaan berasid (62 %) disebabkan adanya kumpulan-kumpulan yang bercas negatif pada permukaan penjerap bio yang mana perlu ada untuk serapan logam itu berterusan dan Cu (II) disingkir sangat banyak dalam masa 40 minit berikutan permukaan serapan pada tumbuhan. Penyelidikan ini telah membuktikan bahawa keladi bunting adalah sangat berkebolehan dalam menyingkirkan Cu (II) dan penjerap bio yang sangat bagus kerana kos yang rendah dan secara tidak langsung mampu menyelesaikan masalah alam sekitar yang dihasilkan oleh tumbuhan yang senang tumbuh ini dan penjerapan bio adalah teknologi yang sangat cekap untuk menggantikan kaedah rawatan tradisional dalam merawat air buangan.

TABLE OF CONTENTS

LIST OF TABLE

LIST OF FIGURE

LIST OF SYMBOLS

μm	-	Micrometer
nm		Nanometer
mA		Miliampere
g	-	Gram
^{o}C	-	Degree Celsius
h	-	Hour
%	-	Percent
C_i	-	Initial Concentration
C_o	-	Equilibrium Concentration

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The contamination of waste water by heavy metal ions is a worldwide environmental problem due to their incremental accumulation in the food chain and continued persistence in the ecosystem (Fatma Ekmekyapar et al., 2006). The main sources of pollution are released into environmental from different activities such as industrial, mining, agricultural activities and etc. Heavy metals are discharged in small quantities into environment through numerous industrial activities. Heavy metals such as chromium, copper, lead, nickel in wastewater are hazardous to the environment and health.

Copper present in industrial wastes is primarily in the form of the bivalent Cu (II) as a hydrolysis product, $CuCO_3$ or organic complexes. The presence of Cu (II) ions in water may cause toxic and harmful effects to the living organisms present and as well as to consumers. Several industries, for example, dyeing, paper, petroleum, copper/brass-plating and copper–ammonium rayon, release undesired amounts of Cu (II). In the copper-cleaning, copper plating and metal-processing industries, Cu (II) concentrations approach 100–120 mg/l. This value is very high in relation to water quality standards and Cu (II) concentrations of wastewaters should be reduced to a value of 1.0–1.5 mg/l (Fatma Ekmekyapar et al., 2006). Common symptoms of copper toxicity are injury to red blood cells, lung and also damage to liver (Cyle Keith et al., 2006). As for copper (II) oxide it is an irritant metal and it can cause damage to the endocrine and central nervous system in human body.

Biosorption can be an effective process and considered as an alternative technology in industrial wastewater treatment for the removal of heavy metal ions from aqueous solutions. It is a method that used aquatic plant as the medium process for treatment. Adsorbent materials (biosorbents) derived from suitable biomass can be used for the effective removal and recovery of heavy metal ions from wastewater streams. The major advantages of biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent materials.

Aquatic plants such as water hyacinth (*Eichhornia crassipes)*, *Thiobacillus ferrooxidans, Fucus serratus, erythrodontium barteri*, *Cladonia rangiformis* hoffm and etc, are known to be effective in this process of treatment. Water hyacinth is one of the most productive plants. This species has rapidly spread throughout inland and coastal freshwater bays and lakes. The root of plant was found to be an excellent accumulator of divalent heavy metal ions from solution through the entire biomass of the plant was also found to be a good sorbent for these ions.

According to Shao-Wei Liao, 2004, water hyacinth is able to adsorb and translocate the cadmium (Cd), lead (Pb), copper (Cu), zinc (Zn), and nickel (Ni) in the plant's tissue as a root or shoot. However, it is 3 to 15 times better to locate the elements into the roots than the shoots. Water hyacinth plants had high bioconcentration with low concentrations of the five elements. This shows that water hyacinth can be a promising candidate to remove the heavy metals.

1.2 Problem Statement

Copper is not biodegradable and tend to accumulate in living organisms (N.A. Adesola Babarinde et al., 2007). It is not acutely toxic, but it can be potentially serious if high levels are present in drinking water. In this paper, copper is the main interest in this study that is used in most industrial or electroplating. Conventional methods for removing heavy metals from industrial effluents such as precipitation and sludge separation, chemical oxidation or reduction, ion exchange, reverse osmosis, membrane separation, electrochemical treatment and evaporation are often ineffective and costly when applied to dilute and very dilute effluents (Mohammad Hassan Khani et al., 2005). Due to this problem, biosorption is the best method as it is economical and indirectly solves another problem. Researcher found other alternative way which will give low cost but high quality in removal of heavy metal in aqueous solution by using water hyacinth. As in this study, water hyacinth been chosen as biosorbent to remove copper (II) in aqueous solution. This species has rapidly spread throughout the lake, rivers, and streams easily. The root is known to act as a cheap biosorbent for various materials which are soluble in water. It can cause enormous ecological and economical damage when it is not controlled. Since it is easy to growth, it can block an irrigation system and give some problem to human. Water hyacinth can reduce diversity, so it is good to use water hyacinth as an adsorbent in order to make it useful than be an environmental problem. Therefore, water hyacinth has become the biosorbent in solving this waste water problem. The dried of water hyacinth can make it simply stored and placed in simple bags as it become powder and used in a very low cost metal ion removal system.

1.3 Objectives

The goals of this study are:

- To investigate the ability of water hyacinth as biosorbent
- To study the biosorption of Copper(II) using dried water hyacinth
- To identify the optimum condition in the removal of heavy metal ions by using dried water hyacinth.

1.4 Scope of Study

There are four scope of study:

- Effect of biosorbent dosage
- Effect of pH
- Effect of time
- Effect of initial concentration

1.5 Rationale and Significant

This study is about to remove Copper (II) that is one of the heavy metals which cause an environmental pollution. These heavy metals cannot be destroyed as they are not biodegradable. It means that the pollution will continuously happen if there is no immediate action been taken and indirectly people or living will expose to the dangerous of heavy metal. They can easily spread out by the wind, food, sources of water and air. So it is rational for us to do the study and remove these heavy metals. Natural materials such as water hyacinth are known as potential plant especially to adsorb the Copper (II) (Shao-Wei Liow et al., 2004). Water hyacinth is a good biosorbent besides we indirectly solve the problem that cause by the multiply very quickly growth of this plant such as reduce the place for mosquitoes to live. Biosorption is the alternative method to remove the heavy metals instead of the conventional method such as ion exchange, reverse osmosis etc and it is such an economical method.

CHAPTER 2

LITERATURE REVIEW

2.1 Heavy Metals

2.1.1 Introduction

Industrial wastewaters, which have heavy metals, are an important source of environmental pollution. These industrialization and urbanization have led to an increase in metal contamination of aquatic environments. Pb, Cd, Cu, Hg, Cr, Ni, and Zn are the main trace elements that are the most harmful to public health. (Sabriye Doyurum et al., 2006). The increased amount of heavy metals has resulted in toxicity of soil, air and water (Corradi et al., 1995). Unlike organic pollutants, which in most cases can eventually be destroyed, metallic species released into the environment tend to persist indefinitely. They circulate and eventually accumulate throughout the food chain, thus posing a series of threats to animals and man. During recent years, the intensive industrial activities, such as electroplating, microelectronics, battery manufacture, dyestuff, chemical, metallurgical, pharmaceutical (Corneliu Cojocaru et al., 2008), metal plating, metallurgical alloying, ceramics, photography (A.T. Al-fawwaz et al., 2008) and other, greatly contribute to the increase of heavy metals in the environment.

In this study, copper (II) is the major concern as it acutely toxic if appear with high level in drinking water. Copper, as native copper, is one of the few metals to naturally occur as an un-compounded mineral. It can be adsorbed by living or non-living biomass (O. Keskinkan et al., 2003). There are several industries are responsible for polluting the environment with high level of heavy metals ions especially copper. These industries and operations may include the metal plating, photograph, pigment works, textile printing industries, lead mining and sewage sludge, alkaline batteries and electroplating (Zaid Ahmed Al-Anber et al., 2007). It will exposed humans to the dangerous of copper. Heavy metals also enter the water supply by industrial and consumer waste or even from acid rain breaking down soils and rocks and releasing heavy metals into streams, lakes, and ground water.

The most important features that distinguish heavy metals from other toxic pollutants are their non bio-degradability. The toxicity due to metal ion is owing to their ability to bind with protein molecules and prevent replication of DNA and subsequent cell division. To avoid health hazards, it is essential to remove these toxic heavy metals from wastewater before its disposal (Elankumaran R. et al., 2003).

2.2 Copper

Copper has a reddish, orangish, or brownish color because a thin layer of tarnish (including oxides) gradually forms on its surface when gases (especially oxygen) in the air react with it. But pure copper, when fresh, is actually a pinkish or peachy metal. It can be found as native copper in mineral form (for example, in Michigan's Keewenaw Peninsula). Minerals such as the sulfides, that are chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), covellite (CuS), chalcocite (Cu_2S) are sources of copper, and as for carbonates such as azurite ($Cu_3(CO_3)_2(OH)_2$) and malachite ($Cu_2CO_3(OH)_2$) and the oxide is cuprite (Cu_2O). Copper is a metal that does not react with water but the oxygen of the air will react slowly at room temperature to form a layer of brown-black copper oxide on copper metal.

Copper (II) oxide is the higher oxide of copper. It is a black solid with an ionic structure which melts above 1200 °C with some loss of oxygen. It can be formed by heating copper in air, but can also formed along with copper(I) oxide; thus, it is better prepared by heating copper(II) nitrate, copper(II) hydroxide or copper(II) carbonate. If it contact to the skin can cause irritation and discoloration. Ingesting cupric oxide can lead to central nervous system depression, liver and kidney damage, gastro-intestinal damage.

It is use in the production of a large variety of alloys having multiple applications, in the electrical industry, in the construction industry such as gas lines, in pigments such as emerald green, in ceramic glazes, and as a salt in the lithographic process and it can be use as pesticides (seeds and vineyards) in the form of salts, like the Bordeaux solution based on copper sulfate.

Copper can be acutely toxic to gastrointestinal tract, eye, renal system, neurologic system and hematologic system. It can also be chronically toxic to the skin, eye, respiratory system and vineyard sprayer's lung. Copper causes a greenish coloration of skin, nails, hair and teeth. Contact dermatitis (copper itch) due to copper is rare and its occurrence can be substantiated by careful patch testing. Eczematous dermatitis and urticaria have been associated with the use of copper intrauterine devices. Long-term exposure to dust in copper refining was not associated with chronic obstructive disease or small airway disease. The higher incidence of respiratory cancer reported in copper smelters is due to the presence of arsenic in the ore.

Vineyard sprayer's lung disease occurred when Bordeaux solution (1 to 2% solution of copper sulfate neutralized with lime) was chronically sprayed by Portuguese vineyard workers. The clinical picture is characterized initially by general symptoms such as weakness, loss of appetite, loss of weight, dyspnea and cough. However, copper also essential for good health and is required for several physiological functions. It is very important to the bones and connective tissue, energy production in the cells, immune system, the glandular system, particularly the thyroid and adrenal glands, reproductive system and nervous system.

2.3 Conventional Method of Waste Treatment

The stringent limits of different pollutant concentrations in industrial and municipal wastewaters, imposed by the environmental legislation, make the treatment to be imperative. Conventional methods for removing of metal ions from aqueous solutions, like chemical precipitation, ion exchange, electrochemical treatment, and adsorption on activated carbon. These techniques are sometimes restricted because of technical or economic constraints as a result of high capital and operational cost. Chemical precipitation and electrochemical treatment become ineffective particularly when metal ion concentration in the solution is low (in the range from 10 to 100 mg/L), because they produce large quantity of sludge to be treated and which require disposal.

Ion exchange and activated carbon adsorption are extremely expensive processes, especially for the treatment of a large amount of wastewater containing low heavy metal concentrations (Corneliu Cojoraru et al., 2008). It is well known technology and commercially available. Unfortunately, high costing will be needed in order to fulfill the required of the ion exchange as it needs replacement after four or five regeneration (Dinesh Mohan et al., 2007).

Adsorption is one type of process that can also treat waste water. It was first found by Lowitz in 1978 and first applied to a process that removes color from sugar refining (Alaa H. Hawari et al., 2005). In 1929, first granular activated carbon (GAC) units of treatment of water supplies that constructed in Hamm, Germany and 1930, at Bay City, Michigan. However high cost of activated carbon limits is use in adsorption. These disadvantages of conventional methods together with the need of more effective and low-cost methods for the metal ions removal from wastewater resulted in the development of new separation technologies. A search for an easily adsorbent has led to the investigation of materials of environmental as potential metal sorbent. In order to reduce the cost of removal of heavy metals, biosorption is potentially an attractive and unique technology for waste water treatment for removing heavy metals using aqueous solution.

2.4 Biosorption

In the copper plating, copper-cleaning and metal processing industrial, Cu (II) concentrations approach 100-120 mg/L, and this value is very high in relation to water quality standards and Cu (II) concentration in wastewater to should be reduced to a value of 1-1.5 mg/L. Mining and metallurgical wastewater are considered to be the major sources of heavy metals contamination and the need for economic and effective for the removal of the metals has led to the development of new technologies based on the utilization of biomasses of plant and animal origin, which serve as biosorbents for the removal of heavy metals from industrial effluents. Biosorption of heavy metals from aqueous solution are considered to be the alternative technology in industrial wastewater treatment.

Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake (N. Ahalya et al) from aqueous solution (Alaa H. Hawari et al., 2005). It can also define as the binding the concentration of heavy metals from aqueous solutions. Microorganisms, including algae, bacteria, yeast, fungi, plant leaves have been used as biosorbents for detoxification and recovery of heavy metals from aqueous solutions.

The dangerous of copper has brought researchers to study the biosorption of copper using different kind of biomass, algae, yeast and so on in order to settling down the toxicity of the heavy metals. The percentage removal of copper are 60 % by using dead green microalgae (A.T. Al-fawwaz et al., 2008), 56.9 % using *Cladonia rangiformis* hoffm (Fatma Ekmekyapar et al., 2006), 68 % using water hyacinth (M. M. Al-Subu et al., 2001).

Biosorption uses biomass raw materials which are either abundant (seaweeds) or wastes from other industrial operations (fermentation wastes). The metal-sorbing performance of certain types of biomass can be more or less selective for heavy metals. That depends on type of biomass, the mixture in the solution, the type of biomass preparation and the chemico-physical environment.

The major advantages of biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent materials. Biosorption processes are particularly suitable for the treatment of wastewater streams containing dilute heavy metal ion concentrations or when very low concentrations of heavy metals are required. The advantage of biosorption compared to conventional treatment such as low cost. Water hyacinth natural materials that are available in large quantities or certain waste from agriculture operations may potentially to use as low cost adsorbent as they represent unused resources, widely available and are environmentally friendly (N. T. Abdel-Ghani et al., 2007). The other advantages when using natural materials such as aquatic plants, fungi, algae, bacteria and yeasts are high efficiency, minimization of chemical or biological sludge, regeneration of biosorbent and possibility of metal recovery. Besides, there is no need to use additional nutrient in separating the heavy metals using biosorption.

Biosorption not only treat waste water but it can also used to:

- metal plating and metal finishing operations,
- mining and ore processing operations,
- metal processing (waste recovery),
- battery and accumulator manufacturing operations,
- thermal power generation (coal-fired plants in particular), and etc.

There are several factors that affecting biosorption such as:

- pH -is the most important parameter in biosorption as it will affect the solution chemistry of metals and activity of functional group in biomass.
- concentration - at low concentration, the removal of heavy metal is high (Cyle Keith et al., 2006). In natural aquatic ecosystems, metallic